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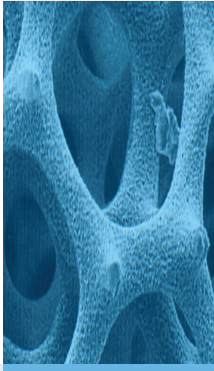
POWDER TECH NOTE 58



# Optimizing Gas Sorption Parameters to Minimize B.E.T. Surface Area Analysis Time

**Material/Application Category:** Porous/Non-porous Solids
**Method Category:** Gas Physisorption (B.E.T.)
**Instrument Category:** Autosorb, Quadrasorb, NOVA

## Introduction

Gas physisorption is the technique by which surface area measurements are made for solid materials; everything ranging from powdered ceramics, pigments to pharmaceutical actives excipients, catalysts, battery and fuel cell materials and carbons.

The technique involve quantitative measurements of adsorption of a gas such as nitrogen onto the surface of the solid as a function of pressure. It is the method used in Quantchrome's Autosorbs (iQ, 6iSA, -1*, 6B*, 3B*), Quadrasorbs (Evo and SI* models) and NOVA instruments. But this adsorption of gas at sub-atmospheric pressures and cryogenic temperatures is a relatively slow process. This can be contrary to the needs of high-throughput or fast analysis requirements often encountered in industry.
** older models still in everyday use.*

## Analysis Variables

For any surface area analysis the user is faced with a number of choices. These include: amount of sample (weight), sample cell type, evacuation speed, whether to check the cell for leaks or not, data point selection ($P/P_O$ range and number of points), equilibration settings (i.e. how slowly must the pressure be changing in the sample cell before a datum point is recorded), how saturation pressure Po is determined, how the void volume is to be determined, and other instrument specific options which determine certain timed functions and how much gas is to be delivered (dosed) to the sample cell at each incremental step. Recommendations are given below on what you can adjust and how to customize these settings to your advantage when analysis speed is important.

## Optimizing Parameters

**SampleAmount:**
The sample amount controls the total surface area in the sample cell – less is faster, more is slower. So a smaller mass of sample will normally analyze more quickly since less gas must be adsorbed in order to cover the surface of the solid. Less mass also thermally equilibrates faster at the cryogenic temperatures needed, and true pressure equilibrium cannot be achieved until the entire sample has been fully cooled and therefore fully capable of adsorbing the gas. However, one must be careful not to analyze too little sample (i) to avoid weighing errors associated with very small sample masses and (ii) not having enough sample to give a representative value due to heterogeneity in the material. If at all possible, aim to use a mass of sample equivalent to the range 1- 20$m^2$ total area when optimizing for speed. 5$m^2$ is a good compromise if you have sufficient material. If you cannot estimate what the surface area might be, start with 0.1g and on subsequent analyses of the same or similar material adjust the sample mass accordingly.

**Recommendation** - use no more than 10$m^2$ in the cell (but never less than 25mg of sample).

**Sample Cell:**
A larger sample cell bulb has a greater void volume and therefore is always dosed with larger amounts of gas. It is sometimes possible to see a reduction in analysis time in this way compared to using a smaller bulb. It is particularly effective when working at very low pressures, e.g. micropore size distribution, and where large mesopore volumes must be filled, but can still be usefully employed in the BET analysis, especially when using lower $P/P_O$ values (see below). Always use a filler rod.

**Recommendation** - use a large bulb cell if you have at least 5$m^2$ in the cell.

**Evacuation Speed:**
The user can select how the sample should be evacuated at the very start of the analysis (for in these types of measurements the sample cell must always be evacuated). If your instrument control software refers to "Fine" evacuation this means a slow reduction of pressure in the cell so as not to elutriate fine powder out of the cell. "Coarse" evacuation means rapid reduction of pressure and the software might offer the choice of pressure at which to change (crossover) from slow (fine) evacuation to fast (coarse). If your sample is pelletized and has no dust, select the highest "crossover" pressure allowed. Some instrument control software simply refers to sample type rather than offering crossover pressure.

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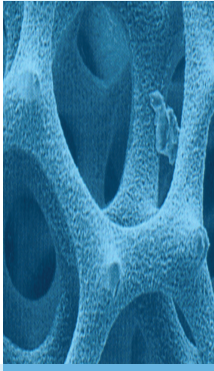

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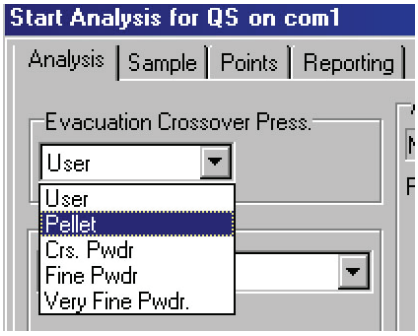


**Recommendation** - use the "coarsest" setting compatible with your sample type.

**Leak Check**

Some instruments like the Autosorb®-iQ require a leak check of the cell before the analysis starts. While this can be crucial for the most exacting low pressure analyses in micropore size measurements, it is far less critical in simple surface area measurements using nitrogen (very low surface area measurements using krypton are more critical in this regard). If you are confident that your sample has been properly outgassed, simply select the shortest time allowed, or dispense with it altogether by choosing an accelerated mode of analysis (if offered, see instruments below).

**Recommendation** - switch leak check off.

**$P/P_O$ Range**

A multipoint BET surface area requires at least three data points but could have as many as seven or more. Fewer points require less cumulative time for equilibration (see Equilibration Settings below for more detail). More points generally allows for greater confidence in calculating the correlation coefficient of the BET plot, but in many cases it's simply not necessary to use more than three so long as the correct $P/P_O$ range is used. Working at lower pressures means that less adsorbate need be adsorbed, resulting in shorter equilibration and analysis times. If the normal BET range were used, say 6 points from 0.05 to 0.3, and the first three points lie on the straight line of the BET plot, there is no need to measure the last three points. Similarly, a pharmaceutical material might only exhibit linearity at the higher end of the BET range, therefore there's no need to analyze the lower points (some extra care might be needed to ensure acceptable equilibration time however).

**Recommendation** - use the following $P/P_O$ points – 0.05, 0.1, 0.15. This range may need to be adjusted to maintain linearity in the BET plot. See Technote#54 for more information regarding microporous materials. Pharmaceutical materials and other weakly adsorbing organics may need the higher (classical) $P/P_O$ range: 0.1, 0.2, 0.3.

**Equilibration Settings:**

The quality of gas physisorption data relies on how well the adsorbed gas on the solid surface is in equilibrium with the gas in the void volume. That usually takes some time, and the user is asked to define equilibrium in terms of rate of pressure change. That is, when the instrument observes a rate of pressure change which is below that defined, the system is understood to be sufficiently well equilibrated, a datum point is recorded and the analyzer proceeds to the next point needed. However, too short a time or not low enough a rate can result in under-equilibrated data and consequently lower than expected surface area values. Additionally the user might be able to set a maximum time in which equilibrium must be achieved. If an excessively long time is chosen here then little is to be gained except an unnecessarily long analysis time.

**Recommendations** -
**Autosorbs**, Eq=2, Tol=3
**Quadrasorb,** Tol.=0.05, Equ=30, Timeout= 90
**NOVA,** Pressure tolerance = 0.05, Equilibration time = 30, Equil. timeout = 90

| $P_O$ (Torr) | Alumina ($m^2/g$): BET 'c' ~100 $P/P_O$ range 0.05 – 0.15 | Titania ($m^2/g$): BET 'c' ~35 $P/P_O$ range 0.15 – 0.30 |
|---|---|---|
| 755 | 28.152 | 2.420 |
| 760 | 28.197 | 2.431 |
| 765 | 28.243 | 2.441 |
| 770 | 28.287 | 2.451 |
| 775 | 28.331 | 2.461 |
| 780 | 28.375 | 2.471 |
| 785 | 28.418 | 2.481 |

**Table 1.** Example Multipoint BET surface area values (measured using nitrogen at 77.4K) as a function of assumed $P_O$ used in the calculation.

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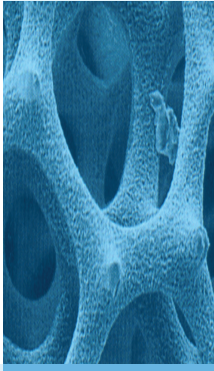

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### Void Volume Method

Volumetric gas sorption measurements rely on knowing how large the void volume is, that is the volume inside the sample cell (and its associated plumbing) not occupied by sample. This can be measured at the time of the analysis after the cell has been evacuated by expanding non-adsorbing gas into the sample cell (so-called classical helium method) or by using a stored value from a helium-free calibration of the cell (the NOVA method [1] – available on Autosorb®-iQ and Quadrasorb™, not just NOVA® instruments).

**Recommendation** - use the NOVA mode if available.

### $P_o$ Determination

The saturation pressure of the gas at the analysis temperature, Po, is used in all BET measurements. It can be (i) measured at run time by liquefying adsorbate in a usually empty cell, (ii) calculated from a measured atmospheric pressure (since it depends largely on ambient pressure), or (iii) input into the program by the user. The first method can take some time (the coolant in the Dewar must be at temperature equilibrium), the second a little time and the last method no time at all. Luckily the BET equation is rather forgiving when it comes to Po values and a very accurate value is not necessary, just a reasonable one that can be quickly estimated from atmospheric pressure (which depends on your elevation above sea level but doesn't change, but can vary with changes in your weather). See **Table 1** for the small differences in results caused by large differences in assumed $P_o$.

**Recommendation** - enter a reasonable estimate for $P_o$ (ambient plus 10 torr).

### NOVA Mode

All current, low-pressure Quantachrome gas sorption instruments can use the helium-free NOVA mode of analysis. Within the NOVA mode the user has a choice whether to correct for sample volume by (i) having the instrument measure the sample volume (by expanding gas like a pycnometer) at the start of the analysis before the dewar is raised or (ii) entering the sample density and have the software calculate the volume based on that and sample weight. Method (i) requires a couple of minutes per sample, while method (ii) takes no time at all. The sample density does not have to be known accurately to three decimals. Most industrial users know exactly what material is being analyzed, so already have the density value.

**Recommendation** – use the 'Calculate Sample Volume' function.

### Quadrasorb evo™

The Quadrasorb evo™ has a QuickMode™ which significantly shortens overall analysis time. This mode automatically switches off any leak checking, uses the previously measured and stored transducer zero, uses a minimum thermal delay (cooling down time after dewar bath comes up) prevents other analyses from being started on unused ports while Quick Mode™ runs are still in progress, causes completed analyses to wait until all Quick Mode™ runs are complete before the dewar is lowered and the sample cell evacuated. When combined with other time saving settings it is not unusal to complete four BET surface area analyses in half the usual time.

**Recommendation** – use QuicMode™.

### NOVA® Instrument

The NOVA® allows you to select a thermal delay (the time after the dewar bath comes up before the next step in the analysis occurs) mainly due to the fact that up to four sample cells can be in the one dewar, not one dewar per sample like the Quadrasorb™. Unless analyzing a large mass of metal powder for example it should not be necessary to use anything more than 180 seconds.

**Recommendation** – use the shortest thermal delay time allowed.

| Material | Density (g/cm³) |
|---|---|
| Alumina (α) | 3.95 |
| Alumina (γ) | 3.65 |
| Carbon (graphite) | 2.2 |
| Carbon (black) | 1.9 |
| Carbon (generic) | 2.0 |
| Silica | 2.65 |
| Titania (rutile) | 4.25 |
| Titania (anatase) | 3.9 |
| Titania (generic) | 4.0 |

◂ **Table 2.** Some typical densities for commonly encountered industrial materials.

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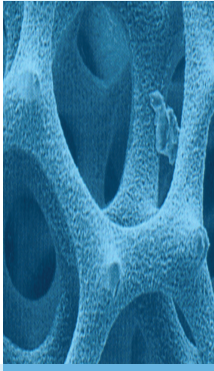

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**Autosorb® Instruments**
The control software in the Autosorb family allows the user to switch off an intelligent algorithm that increases the amount of gas dosed to the sample based on how much is being adsorbed how quickly. It is called Maxidose™. (The NOVA® and Quadrasorb™ also have intelligent algorithms but by default they are always used).

**Recommendation**- leave Maxidose™ switched On.

## Summary

When speed is important there are ways to set up an analysis that will save a significant amount of time.

All sample types are different and the amount of time that can be saved without loss of accuracy will vary; some materials might require a longer cool-down time (thermal delay), others a little bit more sample mass, others somewhat longer equilibration times.

But for the minimum time try the following:

| Parameter | Value |
|---|---|
| Sample amount | 5$m^2$ in the cell |
| Sample Cell | Large bulb |
| Evacuation | As fast as sample particle size will allow |
| BET points (number) | 3 |
| $P/P_O$ values* | 0.05, 0.1, 0.15 |
| Equilibration settings | See text |
| Void vaolume method | NOVA mode[1] |
| [1] Sample volume | Enter density |
| $P_O$ type | Enter value |
| Quadrasorb evo | Quick Mode |
| Nova instruments | Thermal delay <200 |
| Autosorb | Maxidose ON |

**Table 3.** Recommended parameter settings to optimize your analyses for speed†.

*0.05 – 0.3 is the classical BET range and some materials will require data over this entire range. Microporous materials like zeolites should be analyzed in the range 0.05 – 0.075 or lower (see Technote #54). Pharmaceutical materials and other organic materials may require data points 0.1, 0.2, 0.3 for sufficient linearity of the BET plot - or even shifted slightly higher, e.g. 0.15, 0.225, 0.3.

†The above recommendations may or may not be perfectly suited for all sample types. However, the parameters listed are those that you can adjust in order to shorten analysis times. Certain analyses of very low surface areas, weakly adsorbing surfaces, diffusion limited pore structures etc, might require a little more time to produce the accuracy and precision you desire.

**Refer to your instrument's user manual for details on how to access the different setup features mentioned.**

## Reference

**1**. US patent 5,360,743 (Method for measuring a sample sorption and a sample cell void volume and wall adsorption using an adsorbate gas)

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